



Short communication

Heat treatment of LiCoO_2 recovered from cathode scraps with solvent method

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H I G H L I G H T S

- The effects of heat treatment on scrap materials are investigated for the first time.
- After heat-treated, discharge capacity and capacity retention rate are improved.
- recovery method This is low-cost, high recovery rate and environmental friendly.
- Acetylene black and Al foil can be recovered at the same time with this method.

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A B S T R A C T

Solvent method was used to recover LiCoO_2 scrap materials, and the effects of heat treatment on the scrap materials for Li-ion battery were investigated in detail. SEM results showed that heat treatment could slightly reduce the degree agglomeration of the scrap materials. XRD results showed that the layer structure of LiCoO_2 was partly destroyed during the recovery process. Low temperature heat treatment could contribute to restore the original layer structure of LiCoO_2 , however, high temperature heat treatment could lead to the further damage of the layer structure. Compared with the unheat-treated scrap materials, the discharge capacity and the cycle life of the pristine scrap materials heat-treated at 200 °C, 250 °C and 300 °C were obviously improved, Especially after heat-treated at 250 °C, the discharge capacity could reach about 154.6 mAh g⁻¹ and the capacity retention rate still remained at 92.0% after 360 cycles. Particle size distribution, tap density and recovery rate of scrap materials were also investigated.

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1. Introduction

The increased demand for Li-ion batteries (LIBs) has greatly stimulated its production in recent years. Except for a large amount of spent LIBs after use, the electrode scraps generated in the production process of LIBs are also dramatically increasing. Therefore, the recovery and recycle of spent LIBs and electrode scraps attract more and more attention. At present, the conventional recovery process of spent LIBs aims to abstract noble metals (such as Co, Ni and Li) by extraction method, chemical precipitation method or electrolytic method, and the electrode scraps (mainly cathode scraps) are recovered and recycled with the same process [1–16].

These conventional recovery processes are efficient, but there are still many problems. Firstly, they could lead to serious resource waste and environmental pollution because a large amount of acid, alkali and organic solvent are used. Secondly, because of the high recovery cost, these conventional recovery processes are only suitable for the recovery of scraps contained noble metals (such as LiCoO_2 , $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y})\text{O}_2$), but not suitable for LiFePO_4 or LiMn_2O_4 scraps in which there are no noble metals.

Different from spent LIBs, the cathode scraps generated in the production process have not been undergone the charge–discharge process, so the scrap materials can be directly reused only after removing Polyvinylidene Fluoride (PVDF) in scraps and separating down from Al foil with a suitable method. Sintering method is once used to remove PVDF and acetylene black in cathode scraps, but HF from the decomposition of PVDF leads to the decomposition of active material during sintering method, because HF can react with

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active material. So the obtained scrap materials display poor electrochemical performance compared with the unused material [17]. Therefore, developing a new, simply-operated, low-cost, highly-pure, high recovery rate and green recovery method of cathode scrap materials has importantly economic and social significance. Now LiCoO_2 material occupies a large proportion of cathode materials in market, so the recovery research on LiCoO_2 scraps is representative for other cathode scraps.

Herein, in order to study the recovery and heat treatment on the LiCoO_2 scrap material for Li-ion battery, a new solvent method with inexpensive mixture of *N,N*-Dimethylformamide (DMF) and ethanol was used to remove PVDF and recover scrap materials from LiCoO_2 scraps. Structure, electrochemical performances, particle size distribution, tap density and recovery rate of recovered scrap materials were investigated in detail.

2. Experimental

2.1. Preparation

2.1.1. Solvent method

Fig. 1 shows the flowchart of the recovery process with solvent method. 200 g LiCoO_2 scraps (from Tianjin Lishen Battery Joint-Stock Co., Ltd.) were cut up to 4 cm^2 size pieces and added into a 500 mL beaker with 400 mL mixture of DMF and ethanol (8:2 by volume, adding ethanol to DMF could reduce dispersion of scrap materials in DMF, which is convenient for filtering) in batches, and the temperature was maintained at 70 °C. After stirring for 1 h, PVDF was dissolved by DMF and LiCoO_2 scrap materials fell from Al foil, then all the solid–liquid mixtures were filtered and liquid filtrate (mixture of DMF and ethanol) was collected for reuse. The solid residue was dried at 80 °C and heat-treated in air at 200 °C, 250 °C, 300 °C and 350 °C for 1 h, respectively, then solid residue was ball-milled for 0.5 h and smashed and sieved by a 300 mesh screen to separate LiCoO_2 scrap materials from Al foil.

In order to enhance the recovery rate of scrap materials and the purity of Al foil, the separated Al foil was treated again as above recovery method.

2.1.2. Recovery rate of scrap materials

Most of scrap materials (m_1) could be directly recovered after solvent method, but a small amount of the scrap materials (m_2) still remained on impure Al foil mixtures (m_3) and were wasted. After

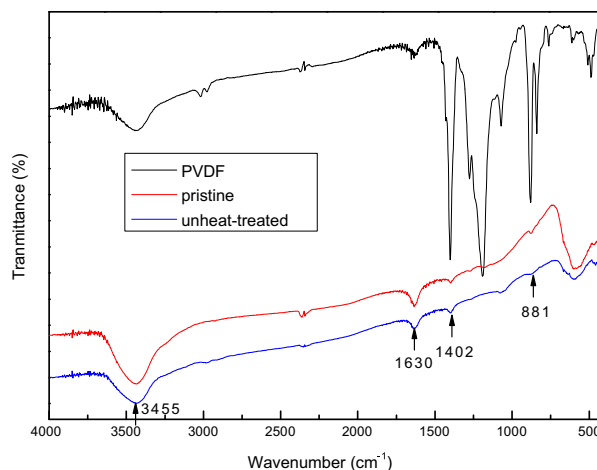


Fig. 2. IR spectra of the unheat-treated scrap materials.

dissolving Al foil mixtures with excessive NaOH solution, the wasted scrap materials (m_2) could be weighed. So the recovery rate of scrap materials with solvent method was $m_1/(m_1 + m_2)$, and the purity of obtained Al foil mixtures was $(m_3 - m_2)/m_3$.

2.2. Compositional and structural characterization

The crystal structure and surface configuration of the scrap materials were characterized by infrared spectrometer (FTIR-650), thermal gravimetric analysis (TGA, EXSTAR6000, SEIKO), scanning electron microscope (SEM, JMS-6700F, JEOL), X-ray diffraction (XRD, Rigaku D/MAX-2500). The particle size distribution was measured with a particle size analyzer (OMEC, LS-POP (6)) and the tap density of scrap materials was measured by ZS tap density meter (ZS-201).

2.3. Electrochemical measurements

According to the datas provided by the Tianjin Lishen Battery Joint-Stock Co., Ltd., the slurry for cathode scraps consisted of 93.5 wt.% active materials, 4 wt.% acetylene black and 2.5 wt.% PVDF, so the composition of recovered the scrap materials included 95.9 wt.% active materials and 4.1 wt.% acetylene black (Assume that PVDF had been completely removed).

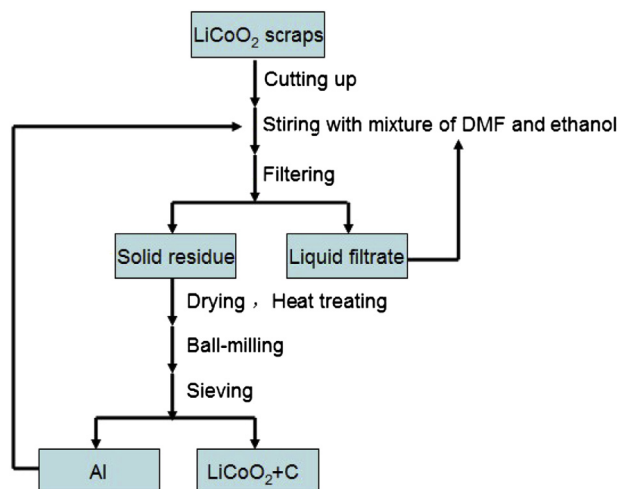


Fig. 1. A flowchart of the recovery process.

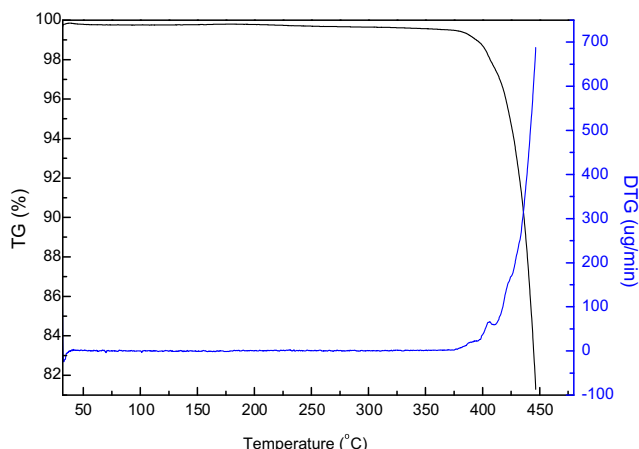


Fig. 3. TG–DTG curve of PVDF.

For fabrication of cathode electrodes consisted of 83 wt.% active materials, 10 wt.% acetylene black, and 7 wt.% PVDF, 3.46 g recovered scrap materials (active materials and acetylene black) were mixed with 0.26 g acetylene black and 0.28 g PVDF in *N*-methyl-2-pyrrolidone (NMP). The electrochemical characterization of electrodes was performed using CR2032 coin-type test cells with lithium foil as the anode and 1 M LiPF₆ in ethylene carbonate and diethyl carbonate (1:1 in volume) as the electrolyte. The cells were charged and discharged between 3.0 V and 4.3 V versus Li⁺/Li by applying a current density of 30 mA g⁻¹ at 25 °C.

3. Results and discussion

3.1. Compositional and structural change of scrap materials

Common solvents which could dissolve PVDF include *N*-methyl-2-pyrrolidone (NMP), Dimethylacetamide (DMAC) and *N,N*-Dimethylformamide (DMF). DMF was chosen in this experiment due to its low cost, high solubility and reusability. Fig. 2 presents IR spectrums of the unheat-treated scrap materials recovered with solvent method. It was observed that there were still some weak characteristic absorption peaks of PVDF (such as 1630 cm⁻¹, 1402 cm⁻¹ and 881 cm⁻¹) in unheat-treated scrap materials, indicating that PVDF was not removed completely with solvent method, even if the intensity of PVDF was decreased compared

with that in the pristine scrap materials directly separated from scraps. Considering the crystal form of LiCoO₂ might be partly destroyed during recovery process, heat treatment after recovered was designed to improve the crystal form. On the other hand, HF decomposed from PVDF could react with LiCoO₂ at high temperature, so the low heat treatment temperature was important to avoid or reduce the reaction between LiCoO₂ and HF decomposed from PVDF. From the TG–DTG curve of PVDF in Fig. 3, there was no obvious decomposition of PVDF until 375 °C, so 200 °C, 250 °C, 300 °C and 350 °C were chosen as heat treatment temperature.

SEM images of the scrap materials heat treated at different temperatures are shown in Fig. 4. There were amounts of flocculent PVDF in the pristine scrap materials, which led to the serious agglomeration of the pristine scrap materials. After recovered with the mixture of DMF and ethanol, flocculent PVDF significantly decreased and agglomeration of the unheat-treated scrap materials was reduced, which was consistent with the IR result in Fig. 2. After heat treated and with the heat treatment temperature increasing, flocculent PVDF decreased and became smaller gradually, thus, agglomeration degree of the scrap materials was further reduced.

Fig. 5 shows XRD patterns of the scrap materials heat treated at different temperatures. *I*₀₀₃/*I*₁₀₄ of the pristine scrap materials directly separated from scraps was 2.73. After recovered with the mixture of DMF and ethanol, *I*₀₀₃/*I*₁₀₄ of the unheat-treated scrap materials decreased to 1.78, demonstrating that the layer structure

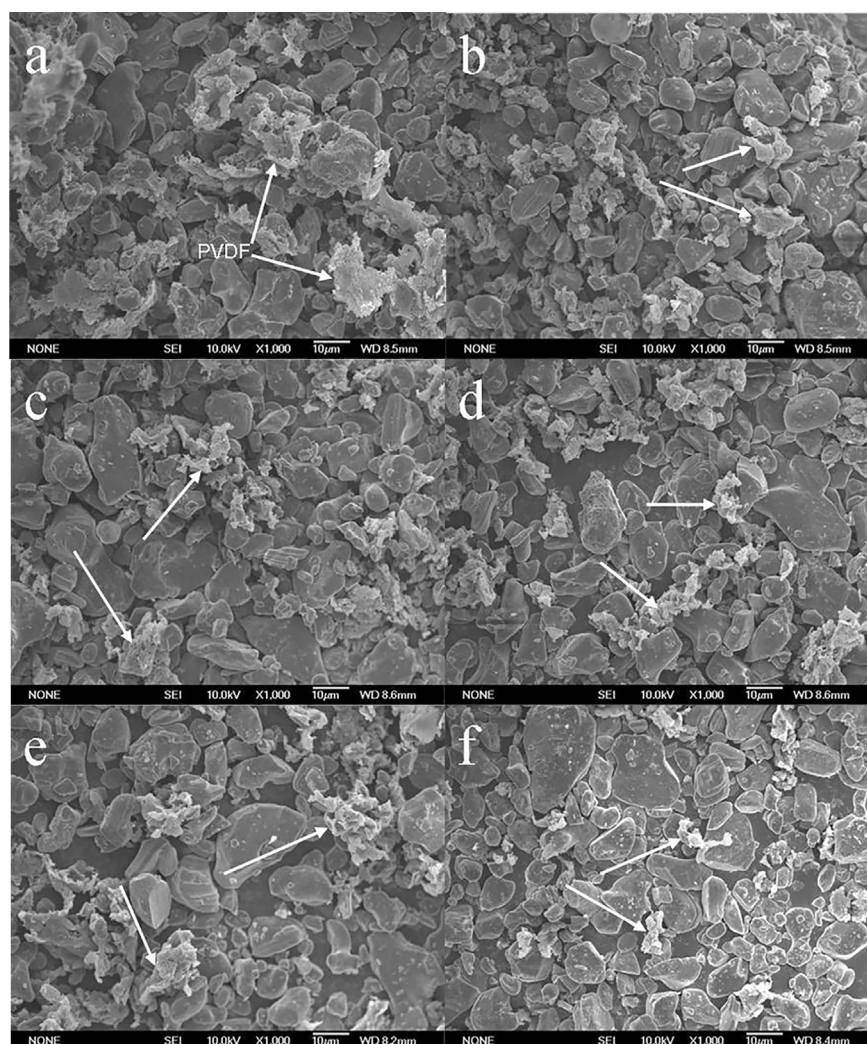


Fig. 4. SEM images of the scrap materials heat treated at different temperatures.

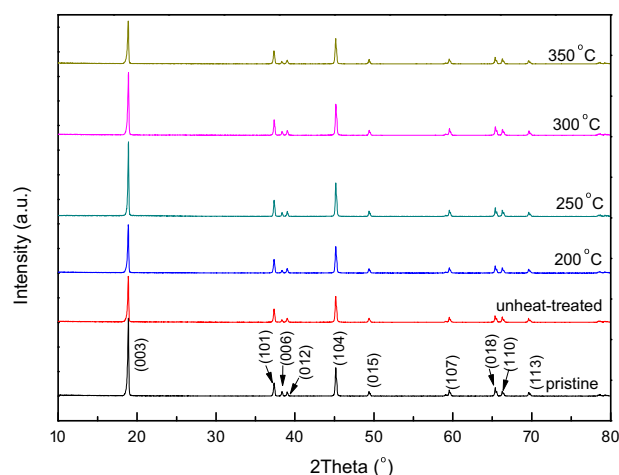


Fig. 5. XRD patterns of the scrap materials heat treated at different temperatures.

of LiCoO_2 was partly destroyed during the recovery process. Whereas, after heat treated, I_{003}/I_{104} increased to 1.81 at 200 °C and 2.21 at 250 °C, but decreased to 2.02 at 300 °C and 1.69 at 350 °C. The changes of I_{003}/I_{104} demonstrated that low temperature heat treatment contributed to restore the original layer structure of LiCoO_2 , but high temperature heat treatment could lead to the further damage of the layer structure. Considering that self-decomposition or carbothermal reduction reaction could not occur at this temperature and PVDF was not removed completely with solvent method, so the main reason for the decrease of I_{003}/I_{104} should be still attributed to HF. During the heat-treated process above 300 °C, a small amount of PVDF decomposed into HF, then LiCoO_2 reacted with HF and generated LiF and cobalt oxide. In order to verify this assumption, scrap materials after heat treatment were washed with hot water, and saturated CaCl_2 solution was used to test the exist of F^- . The appearance of white precipitate (CaF_2) verified that the LiF existed in the scrap materials after heat treatment, which proved the rationality of the above assumption.

3.2. Electrochemical properties of scrap materials

Fig. 6 displays the cycle life of the scrap materials heat treated at different temperatures. Compared with the pristine scrap materials, both the discharge capacity and the cycle life of the unheat-treated scrap materials were poor. After heat-treated at 200 °C,

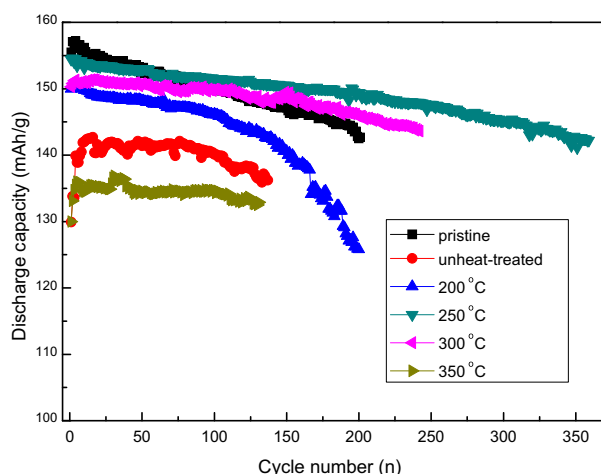


Fig. 6. Cycle life of the scrap materials heat treated at different temperatures.

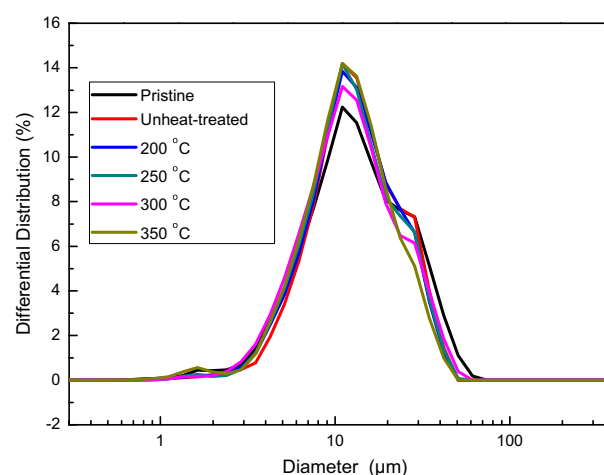


Fig. 7. Size distribution curves of the scrap materials heat treated at different temperatures.

	$D_{10}(\mu\text{m})$	$D_{50}(\mu\text{m})$	$D_{90}(\mu\text{m})$
Pristine	5.73	11.65	28.08
unheat-treated	5.30	11.34	24.80
200 °C	5.07	11.13	24.59
250 °C	5.04	10.96	24.59
300 °C	4.98	10.84	22.85
350 °C	4.96	10.66	22.25

250 °C and 300 °C, respectively, the discharge capacity and the cycle life were obviously improved, compared with the unheat-treated scrap materials. Especially after heat-treated at 250 °C, the discharge capacity could reach about 154.6 mAh g^{-1} (close to that of the pristine scrap materials) and the capacity retention rate still remained at 92.0% after 360 cycles (better than that of the pristine scrap materials). However, the discharge capacity of scrap materials treated at 350 °C was only about 135 mAh g^{-1} , which was far below the pristine scrap materials. It could be seen that the heat treatment at low temperature (200 °C, 250 °C and 300 °C) could improve electrochemical performances of scrap materials and the heat treatment at high temperature (350 °C) could lead to the decomposition of LiCoO_2 caused by HF from PVDF and the poor electrochemical performances. The results were consistent with the XRD results in Fig. 5.

Except for the structure and electrochemical performance, the research about the effects of heat treatment on the particle size distribution and tap density of scrap materials is essential, which are also the important parameters for Li-ion battery cathode materials. Fig. 7 shows the particle size distribution curves of the scrap materials heat treated at different temperatures. Heat treatment had a little effect on the particle size distribution. After recovered,

Table 1

The tap densities of the scrap materials heat treated at different temperatures.

Scrap materials	Tap densities (g cm^{-3})
Pristine	1.797
Unheat-treated	2.067
200 °C	2.099
250 °C	2.117
300 °C	2.121
350 °C	2.168

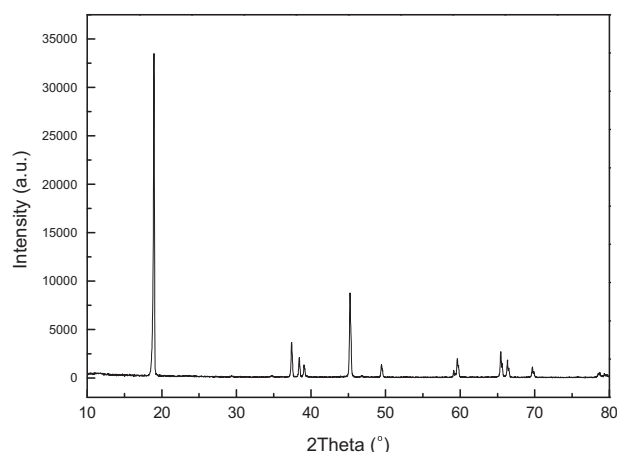


Fig. 8. XRD pattern of the scrap materials obtained from impure Al foil mixtures.

the average particle diameter (D_{50}) of the unheat-treated scrap materials slightly decreased compared with the pristine scrap materials. After heat treated, the average particle diameter gradually decreased with the heat treatment temperature increasing.

The tap densities results are consistent with particle size distribution results. Table 1 lists the tap densities of the scrap materials heat treated at different temperatures. It is obvious that the tap densities of the recovered scrap materials after heat-treated are a little larger than those of both pristine and unheat-treated scrap material, and the tap densities of the recovered scrap materials become larger gradually with the increase of heat treatment temperature. The reason for these changes of tap densities and particle size distribution could be explained as follows. After recovered with the mixture of DMF and ethanol, most PVDF was removed and the agglomeration of particles was reduced, so the average particle diameter decreased and the tap density increased. With the heat treatment temperature increasing, the residual PVDF began to soften and fail, even gradually decomposed, so the agglomeration degree of the scrap materials reduced, the average particle diameter further decreased and the tap density further increased. In addition, after heat treated, the average particle diameter and the tap density of the scrap materials reached the demand for the commercial use.

3.3. Recovery rate of scrap materials

In order to investigate the recovery rate of scrap materials, 200 g LiCoO_2 scraps were recovered with the above solvent method. After the recovery, 145.82 g scrap materials (active material, acetylene black) and 41.86 g impure Al foil mixtures (Al foil, active material, acetylene black) were directly obtained through the first separation. Then, after the second step, 21.60 g scrap materials (active material, acetylene black) were collected from 41.86 g impure Al foil mixtures after dissolving Al foil mixtures with excessive NaOH solution. From Fig. 8, there is no Al(OH)_3 impurity in 21.60 g scrap materials. So the recovery rate of scrap materials is $145.82 / (145.82 + 21.60) \times 100\% = 87.10\%$, and the purity of Al foil mixtures is $(41.86 - 21.60) / 41.86 \times 100\% = 48.40\%$.

In order to improve the recovery rate of scrap materials, the obtained impure Al foil mixtures were recovered with the solvent method again. After calculation, the recovery rate of scrap materials increased to 91.88% and the purity of Al foil increased to 59.83% after two step recovery processes. The high recovery rate of scrap materials and the high purity of Al foil make this recovery method feasible in practice.

3.4. Economic analysis

Compared with the conventional recovery process, the new solvent method is significantly simplified and simply operated. The mixture of DMF and ethanol could be reused during recovery process until saturation, saturated DMF + ethanol mixtures were also not worthless and wasted. After vacuum distillation, PVDF, DMF and ethanol could be recovered from saturated DMF + ethanol mixtures, respectively. During the whole recovery process, there is no pollutant discharge into environment, so this new solvent method is low-cost and environmental friendly. At last, acetylene black and Al foil were also recovered at the same time with this method, which further enhanced the recovery added-value.

4. Conclusions

LiCoO_2 scrap materials are recovered with solvent method using inexpensive mixture of DMF and ethanol, and the effects of heat treatment on the scrap materials are systematically investigated. The layer structure of LiCoO_2 is partly destroyed during the recovery process. Low temperature heat treatment can contribute to restore the original layer structure of LiCoO_2 , however, high temperature heat treatment can lead to the further damage of the layer structure. The heat treatment at 200 °C, 250 °C and 300 °C can obviously improve electrochemical performances of scrap materials, while the heat treatment at 350 °C can lead to the decomposition of LiCoO_2 caused by HF from PVDF and the poor electrochemical performances. Remarkably, after heat-treated at 250 °C, the discharge capacity and the capacity retention rate are close to or better than those of the pristine scrap materials. Meanwhile, compared with the unheat-treated scrap materials, the heat treatment can decrease the average particle diameter and increase the tap density. The recovery rate of scrap materials can reach 91.88% after two-step recovery processes. This recovery method is simply operated, low-cost, high-purity, high recovery rate and environmental friendly.

Acknowledgments

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References

- [1] L. Li, J. Lu, Y. Ren, X.X. Zhang, R.J. Chen, F. Wu, K. Amine, J. Power Sources 218 (2012) 21–27.
- [2] L. Li, J. Ge, R.J. Chen, F. Wu, S. Chen, X.X. Zhang, Waste Manag. 30 (2010) 2615–2621.
- [3] L. Li, R.J. Chen, F. Sun, F. Wu, J.R. Liu, Hydrometallurgy 108 (2011) 220–225.
- [4] L. Li, J. Ge, F. Wu, R.J. Ch, S. Chen, B.R. Wu, J. Hazard. Mater. 176 (2010) 288–293.
- [5] T. Georgi-Maschler, B. Friedrich, R. Weyhe, H. Heegn, M. Rutz, J. Power Sources 207 (2012) 173–182.
- [6] L. Sun, K.Q. Qiu, J. Hazard. Mater. 194 (2011) 378–384.
- [7] L. Sun, K.Q. Qiu, Waste Manag. 32 (2012) 1575–1582.
- [8] Y. Pranolo, W. Zhang, C.Y. Cheng, Hydrometallurgy 102 (2010) 37–42.
- [9] L. Chen, X.C. Tang, Y. Zhang, L.X. Li, Z.W. Zeng, Y. Zhang, Hydrometallurgy 108 (2011) 80–86.
- [10] J. Kang, J. Sohn, H. Chang, G. Senanayake, S.M. Shin, Adv. Powder Technol. 21 (2010) 175–179.
- [11] J. Kang, G. Senanayake, J. Sohn, S.M. Shin, Hydrometallurgy 100 (2010) 168–171.
- [12] J.M. Nan, D.M. Han, X.X. Zuo, J. Power Sources 152 (2005) 278–284.
- [13] M.K. Jha, A. Kumari, A.K. Jha, V. Kumar, J. Hait, B.D. Pandey, Waste Manag. 33 (2013) 1890–1897.
- [14] M.B.J.G. Freitas, E.M. Garcia, J. Power Sources 171 (2007) 953–959.
- [15] C.K. Lee, K.I. Rhee, Hydrometallurgy 68 (2003) 5–10.
- [16] G. Dorella, M.B. Mansur, J. Power Sources 170 (2007) 210–215.
- [17] D.W. Song, X.Q. Wang, E.L. Zhou, P.Y. Hou, F.X. Guo, L.Q. Zhang, J. Power Sources 232 (2013) 348–352.